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13. ABSTRACT (Maximum 200 words) The evaluation of risk to the environment by subsurface contamination remains one of the major challenges to Army. Numerical models such as the US Army's Groundwater Modeling System that simulate water flow and chemical transport are increasingly used in remediation design and analysis. This research contributes towards a better understanding of field-testing methods to obtain model parameters. The focus was on both reactive and sorptive parameters. The experimental component of the study was conducted in a three-dimensional intermediate-scale test tank to obtain accurate data on behavior of non-reactive and sorptive tracers. This database was used to validate a numerical model, which was then used to analyze behavior over a wider range of scales. A large number of hydraulic and tracer tests were performed in the test aquifer, in three different mean flow configurations – uniform flow, radially divergent and convergent flow. This is a very unique dataset that will be available to other researchers. It will help to evaluate models and stochastic theories of upscaled flow and transport. In a related study, a fundamental theoretical analysis of the relationship between surface properties of rock fractures and effective behavior of transport was carried out. The results of both studies are of theoretical and practical significance.			
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STATEMENT OF THE PROBLEM STUDIED

The evaluation of the risk to humans and the ecological environment by hazardous waste chemicals in soils and groundwater remains one of the major challenges to Army. Numerical models that are designed to simulate the flow of water and transport behavior of chemicals in the subsurface are increasingly used in decision making and risk analysis. These models also can be used in the design of cost-effective remediation schemes and evaluation of strategies for cleanup. The DoD's Groundwater Modeling System is a tool that has gained wide acceptance as a comprehensive flow and transport simulator. This research will contribute towards developing better field-testing methods to obtain the input parameters to be used in these flow and transport simulators.

In field application of numerical transport models, it is necessary provide as inputs, parameters that describe the transport behavior of dissolved chemicals in naturally heterogeneous subsurface where the soil and geologic conditions vary in space. This research focuses on both reactive and sorptive parameters that are used in transport models. The dispersivity characterizes the spread of the dissolved chemical due to mechanical mixing within the formation. The retardation factor characterizes the process by which the dissolved solute species sorb onto the solid materials in the aquifer. As the processes of mixing and sorption are controlled by the formation heterogeneity, it has been found that the field estimated value of dispersivity and sorption coefficients depend on the measurement scale in which effects of the heterogeneity are captured. Transport parameters are estimated in the field by conducting tests that involve injecting a tracer into the aquifer and monitoring the movement of the resulting tracer plume. A type of tracer test that is referred to as a "forced-gradient test" is conducted by injecting the tracer at a well that creates an artificial gradient. In another type of test that is referred to as the "natural-gradient test," the tracer is introduced to the aquifer under existing conditions of natural groundwater flow. The dispersivity values that are estimated from these two methods have found to be different, even though in theory they characterize the same process of dispersion as controlled by the geologic heterogeneity. The main goal of this research is to study the scale dependence of the dispersivity coefficient and retardation related to different flow configurations and source sizes. Experimental and computational investigations were conducted. The experimental component of the study was conducted in intermediate-scale test tanks to obtain accurate date sets on behavior of non-reactive and sorptive tracers. This database was used to validate a numerical model that afterwards was used to conduct further simulation analysis involving a wider range of scales. In a related study, similar issues to those mentioned above were studied in the context of a single fracture, with wall reactions. The important question here is the relationship between the physicochemical properties of fracture surfaces and the effective behavior of transport in the fracture.

SUMMARY OF THE MOST IMPORTANT RESULTS

A. Intermediate-scale experiments on non-reactive and reactive transport in heterogeneous porous media

(The details of these findings that are summarized here can be found in a PhD dissertation Fernàndez-Garcia (2003) and journal articles Fernàndez-Garcia, 2003a- 2003e, which are in preparation).

An intermediate-scale three-dimensional test aquifer was constructed incorporating physical and chemical heterogeneity in medium properties. The structure of heterogeneity was designed to resemble features

observed at well-documented field sites. The variation of medium properties in the test aquifer was specified, based on a computer-generated random field, with a mean value of natural log hydraulic conductivity ($\ln K$) = 4.77 and variance of $\ln K$ = 1.8. The correlation structure of $\ln K$ was anisotropic, with a correlation length of 10.16 cm in the horizontal direction and 2.88 cm in the vertical direction. The overall dimensions of the tank are 101.6 cm x 101.6 cm x 43.18 cm. Five different sand types were used to achieve the desired statistical properties – in this sense the test aquifer represents a discretized version of natural heterogeneous porous media. Consistency between the targeted hydraulic properties in the test aquifer and the values actually realized was verified based on carefully conducted hydraulic tests in uniform and radial flow configurations. These hydraulic tests were then simulated using targeted $\ln K$ fields, and the simulated results were compared to the experimental results. The agreement between simulated and experimental results was very reasonable. This accomplishment is a “proof-of-concept” that it is indeed possible to reliably construct three-dimensional heterogeneous porous media in the laboratory for controlled experimental studies. We believe that ours is the first successful attempt along these lines. The test aquifer can be used in a variety of important applications to address several important generic questions relevant to subsurface contaminant transport – (i) Can large-scale transport be predicted based on a characterization of small-scale property variations? (ii) What type of information on field-scale properties is obtained using different typical tracer test configurations at different scales? Are they mutually consistent? (iii) What are the limits to predictability in flow and transport in heterogeneous aquifers, in the ideal scenario where the heterogeneous structure is completely defined, as in an intermediate-scale constructed test aquifer?

A highly accurate and reliable dataset on flow and transport was generated in the test aquifer. A large number of hydraulic and tracer tests were performed in this aquifer, in three different mean flow configurations – uniform flow, radially divergent flow and radially convergent flow. The uniform flow configuration corresponds to typical natural gradient conditions, and the radial flow configurations correspond to forced-gradient conditions typically encountered in tracer tests used for site characterization. In the reactive tracer tests, Lithium Bromide (LiBr) was used as the tracer. Bromide (Br) served as the non-reactive tracer and Lithium (Li) was adsorbed on the test sands, thus serving as a reactive solute. The hydraulic properties and sorptive properties of Li on the test sands were characterized based on carefully conducted small-scale column experiments. This is a very unique and valuable dataset that will be available to other researchers. It will help to evaluate various types of groundwater flow and transport models, and also to evaluate stochastic theories of upscaled flow and transport.

An approach based on temporal moment analysis was developed for evaluating scale-dependent dispersion under natural gradient (uniform flow) conditions. The technique is generic and a fundamental counterpart based on temporal data at a set of fixed locations, to the more popular approach based on spatial moments involving spatial data at a fixed time. From a theoretical standpoint, an advantage of the temporal moments technique we have proposed, is that no restrictive assumptions on the velocity probability density function or a small value of the variance of $\ln K$ are needed. The advantage of temporal moments in contrast to spatial moments is that the latter requires very extensive three-dimensional sampling of a contaminant plume, whereas the former requires only a battery of deep-penetrating wells intersecting the plume. Thus, from the viewpoint of site characterization, the temporal moments based technique can be extremely cost-effective. The practical value of this technique has been demonstrated based on the experimental data from our three-dimensional test aquifer, data from the Cape Cod tracer test and extensive numerical simulations. The asymptotic dispersivity estimates obtained using the temporal moments technique are shown to be consistent with values obtained using other well established techniques.

A comparison of scale-dependence in effective dispersivities based on temporal moments and spatial moments has been carried out based on carefully designed high-resolution numerical simulations. Our results suggest that whereas the scale-dependent dispersivity based on temporal and spatial moments is identical for small values of the variance of $\ln K$, there are discrepancies at larger values of the variance of $\ln K$ and in statistically anisotropic media. The dispersivity based on temporal moments typically exhibits less pronounced scale-dependence than the dispersivity based on spatial moments, but approaches the same asymptotic value at

large travel distances/times. The theoretical basis for the difference between the different types of dispersivity estimates is demonstrated. The role of nonergodic effects in leading to smaller effective dispersivities for small source sizes are also demonstrated based on numerical simulations.

The temporal moments based approach is also evaluated for analysis of scale-dependent dispersion in uniform and forced-gradient mean flow fields. Analytical expressions for dispersivities based on temporal moments were compared to computational results in homogenous media and showed excellent agreement. In convergent flow tracer tests, the pumped well suffices, while in divergent flow tracer tests, a circle of monitoring wells will be required. Temporal moments based techniques were used to evaluate the scale-dependence of dispersivities inferred from different types of tracer tests in homogeneous and heterogeneous porous media, including an analysis of data from our test aquifer. Results from our test aquifer suggest that dispersivities estimated from uniform flow tracer tests using the temporal moments approach are consistent with stochastic theory at small values of the variance of $\ln K$. However, dispersivities estimated from divergent flow tracer tests are smaller than those estimated from uniform flow tracer tests, even if a deep penetrating injection well is used. Convergent flow tracer tests involving small sources lead to dispersivity values much smaller than those obtained with the other two approaches, due to non-ergodic effects. Extensive numerical simulations were pursued to further clarify the relationship between dispersivities estimated from uniform flow and divergent flow tracer tests over a wider range of scales. These simulation results suggest that at large displacements dispersivities estimated using temporal moments analysis from forced gradient tracer tests involving several simultaneous injections at the same radius, approach the same asymptotic constant value as in uniform flows. However the estimates from forced-gradient tests exhibit a more pronounced scale-dependence, which is consistent with the behavior seen in the test aquifer.

Transport of Lithium in a chemically heterogeneous aquifer was investigated in our three-dimensional test aquifer. The sorptive properties of Lithium on the test sands were characterized using batch and small-scale laboratory column experiments. Lithium sorption was found to be described by a Freundlich isotherm for the five test sands. For all but one of the sands, a robust correlation between column-scale Freundlich parameters and $\ln K$ were noted. Furthermore, the column-scale apparent retardation factor exhibited a robust inverse relationship with $\ln K$ for all but one of the test sands. Forward simulation of reactive transport using the parameters for individual sands estimated from column experiments did not agree well with observed Lithium breakthrough curves. This suggests the limits to predictability of reactive transport using equilibrium adsorption models.

The Lithium transport experiments indicated an enhancement of longitudinal dispersion compared to the conservative tracer (Bromide). The enhancement of longitudinal dispersion was not predicted accurately based on linear models (i.e. using a simple retardation factor to account for sorption). However, the effective retardation factor at the scale of the test aquifer was predicted very well using stochastic theories assuming a linear model (i.e. effective retardation factor = arithmetic mean of individual sand retardation factors). Scale dependence of the effective retardation factor is also qualitatively consistent with stochastic theories.

A theoretical result for the index of enhanced macrodispersivity of a linearly adsorbed solute was developed, which does not require any specific assumptions on local relationships between the retardation factor and $\ln K$. This result is applicable only for the asymptotic macrodispersivity. However, the fact that the dispersivity estimated from temporal moments analysis reaches its asymptotic value within displacements of a few correlation lengths, renders our result very useful.

B. Transport with wall reactions in fractures

(The details of these findings that are summarized here can be found two journal articles Bloechle and Rajaram, 2003 a and 2003 b, which are in preparation)

We have studied the transport of a reactive solute in an individual fracture. In particular, we have considered mathematical models of reactive transport in a two-dimensional, parallel-plate, fracture-matrix system. The models include linear and nonlinear irreversible, instantaneous reversible, and kinetic reversible reactions at the fracture wall as well as diffusion into the matrix surrounding the fracture. Using a variety of analytical methods, we have derived one-dimensional "effective" models that capture the long-time behavior of the average concentration over the fracture cross section. The validity of each effective model was verified by comparing the effective concentration to the average concentration obtained from a numerical solution of the two-dimensional model. The primary results of this research program are summarized below.

We have provided a comprehensive theory of Taylor dispersion for a solute that undergoes either a linear irreversible, instantaneous reversible, or kinetic reversible reaction at the fracture wall. We have demonstrated the efficacy of a mathematical technique known as the "asymptotic spectral comparison method" in deriving effective models for these three cases. We have examined the dependence of the effective parameters on the model parameters and have identified the conditions under which the effective models are valid.

The existing literature on Taylor dispersion focuses on the transport of passive solutes and solutes that undergo linear surface and/or bulk reactions. Little attention has been paid to the effect of nonlinear reactions on the dispersion process. We have presented what is believed to be the first study on the influence of nonlinear surface reactions on Taylor dispersion in fractures. A multiple-scales perturbation approach was used to derive a nonlinear effective model that applies to a large class of weak nonlinear irreversible reactions. The coefficients of the effective equation depend on the average concentration through the reaction rate law and its derivatives. The validity of the nonlinear effective equation for various nth-order and Michaelis-Menten reactions was verified via numerical simulations.

The first steps in analyzing the influence of nonlinear equilibrium adsorption have been taken. We have calculated numerical solutions of the two-dimensional transport model assuming that the solute undergoes Langmuir or Freundlich adsorption at the fracture wall. In the Langmuir adsorption case, the average concentration approaches the effective concentration described by an effective model for linear adsorption. In the Freundlich adsorption case, the average concentration approaches the effective concentration described by an effective model for a nonreactive solute. In both of these cases, the rate at which the average concentration approaches the effective concentration depends on the strength of the nonlinearity. We conjecture that the analytical techniques developed to deal with nonlinear irreversible reactions can be modified to deal with these nonlinear reversible reactions. The resulting nonlinear effective models should more accurately capture the transport process at earlier times during which the linear effective model is inappropriate.

Further analysis of solute transport in a parallel-plate fracture assuming the solute undergoes kinetic adsorption and desorption at the fracture wall has been performed. In the literature, a number of effective models have been derived that describe the asymptotic, long-time behavior of the average concentration over the fracture cross-section. These effective models typically consist of an effective advection-diffusion-reaction equation along with appropriate effective coefficients (effective reaction rate constant, effective velocity, and effective diffusion coefficient) which depend on the various geometrical and physicochemical parameters of the system. After a sufficiently long time has elapsed, the solution of the effective model, the effective concentration, is a good approximation of the average concentration. However, when the rate of adsorption or desorption is slow, the development time may be long, thus rendering the effective model irrelevant. Under these conditions, an effective model that captures the kinetic nature of the process is desirable. We have used the asymptotic spectral comparison method to derive an effective model that captures the kinetic nature of the transport process and is therefore valid at earlier times. We have verified that the resulting effective model more accurately captures the intermediate kinetic nature of the process via numerical simulations. The method

we use to derive the effective model can be extended to other problems that exhibit kinetic-like behavior, for example, passive solute transport in a fracture including the effects of matrix diffusion.

Finally, we have examined the influence of matrix diffusion and linear equilibrium adsorption in the matrix on retardation and dispersion in the fracture-matrix system. The method of moments was used to derive an effective advection-diffusion-retardation equation and time-dependent expressions for the first two longitudinal spatial moments. We examined the influence of the model parameters on the effective parameters, studied the preasymptotic behavior of the spatial moments, and identified the conditions under which the effective equation is a valid approximation to the long-time behavior of the average concentration. The long-time behavior associated with matrix diffusion is analogous to the long-time behavior associated with a kinetic reversible reaction. As a result, we considered a two-phase effective model that allows for kinetic exchange between the phases. The effective parameters are determined by matching the long-time behavior of the spatial moments of the effective concentration to the long-time behavior of the spatial moments of the average concentration.

The results of this research program provide a foundation for further study of reactive transport in fractured porous media. We believe that the mathematical techniques developed can be extended to nonlinear instantaneous and kinetic reversible surface reactions as well as to multispecies reactions in the bulk fluid. The physical insights obtained serve as a basis for the study of reactive transport in more realistic, and more complicated, fractures and fracture networks. We also expect that our results will be of interest to scientists and engineers studying Taylor dispersion in other contexts.

LISTING OF ALL PUBLICATIONS

(a) Papers published in peer-reviewed journals

Barth, Gilbert R.; Illangasekare, Tissa H.; Hill, Mary C.; Rajaram, Harihar, 2001, A new tracer-density criterion for heterogeneous porous media, *Water Resour. Res.* 37(1), 21-32.

Barth, G.R., M. C. Hill, T. H. Illangasekare and H. Rajaram, 2001, Predictive Modeling of Flow and Transport in a Two-Dimensional Intermediate-Scale Heterogeneous Porous Medium, *Water Resources Research* 37 (10) 2503-2512.

Fernàndez-Garcia, D., Sánchez-Vila, X., Illangasekare, T. H., 2002. Convergent-flow tracer tests in heterogeneous media: combined experimental-numerical analysis for determination of equivalent transport parameters. *J. Contaminant. Hydrology*, 57, 129-145.

(b) Papers in conference proceedings

None

(c) Papers presented at meetings

B. W. Bloechle and H. Rajaram, "An Effective Two-Phase Kinetic Model of Solute Transport in an Individual Fracture," Fourth Annual VIGRE Symposium, Department of Applied Mathematics, University of Colorado at Boulder, Boulder, CO, July 26, 2002.

B. W. Bloechle and H. Rajaram, "The Influence of Nonlinear Irreversible Surface Reactions on Taylor Dispersion in an Individual Fracture," Third Annual VIGRE Symposium, Department of Applied Mathematics, University of Colorado at Boulder, Boulder, CO, July 20 and 26, 2001.

B. W. Bloechle and H. Rajaram, "The Influence of Nonlinear Irreversible Surface Reactions on Taylor Dispersion in an Individual Fracture," Sixth SIAM Conference on Mathematical and Computational Issues in the Geosciences, Boulder, CO, June 11-14, 2001.

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Fernàndez-Garcia, D., Illangasekare, T. H., Rajaram, H., 2002. Laboratory sorptive and non-reactive tracer tests in a highly heterogeneous synthetic aquifer. *Denver 2002 GSA Annual Meeting*, Denver, Colorado. Oral presentation.

(d) Papers in preparation to be submitted

B. W. Bloechle and H. Rajaram, "An Effective Two-Phase Kinetic Model of Solute Transport in an Individual Fracture," to be submitted to Water Resources Research.

B. W. Bloechle and H. Rajaram, "The Influence of Nonlinear Irreversible Surface Reactions on Taylor Dispersion in a Parallel-Plate Channel," to be submitted to Chemical Engineering Science.

Fernàndez-Garcia, D., Illangasekare, T. H., Rajaram, H., 2003a. Scale-dependence of dispersivity estimated from temporal moments in heterogeneous porous media. Manuscript in progress for submission in 2003.

Fernàndez-Garcia, D., Illangasekare, T. H., Rajaram, H., 2003b. Intermediate-scale laboratory reactive tracer tests in a physically and chemically heterogeneous three-dimensional test aquifer: Uniform flow and performance of stochastic theories. Manuscript in progress for submission in 2003.

Fernàndez-Garcia, D., Illangasekare, T. H., Rajaram, H., 2003c. Influence of the flow configuration on conservative and reactive transport parameters estimated from field tracer tests: Laboratory tracer tests in a 3-D test aquifer. Manuscript in progress for submission in 2003.

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3. Daniel Fernàndez-Garcia- Colorado Schooll of Mines, PhD degree to be granted in May 2003.
4. Brian W. Bloechle- University of Colorado, PhD degree granted in May 2002.

INVENTIONS

None

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